

OPTICAL RADIATION FROM THE INTERACTION OF ENERGETIC ATOMS, IONS, ELECTRONS, AND PHOTONS WITH SURFACES

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Abstract. Heavy particle, electron, and UV photon bombardment of solid surfaces has been recently observed to result in the emission of infrared, visible, and ultraviolet radiation. This effect occurs over a wide range of incident projectile energies. Line radiation arising from transitions between discrete atomic or molecular levels may be attributed to the decay of excited particles which have been sputtered or electronically/chemically desorbed from the surface. Broadband continuum radiation, which is also observed, is believed to arise either from fluorescence of the near surface bulk or from the radiative decay of desorbed excited clusters. The spectral characteristics of the optical radiation as well as the efficiencies for producing it may vary substantially with the identity, form and cleanliness of the surface, and on the identity and energy of the bombarding particle. Spacecraft, in the ambient near-Earth environment, are subject to such bombardment. The dynamics of energetic particle and photon beam interactions with surfaces which lead to surface erosion and glow phenomena will be treated. In addition, projected experimental and theoretical studies of oxygen and nitrogen beam-surface interactions on materials characteristic of spacecraft surfaces will be discussed.

Introduction

Exterior surfaces of spacecraft in near-Earth orbit are bombarded by a formidable assortment of neutral and ionized atoms and molecules, in addition to electrons and ultraviolet photons. Heavy particle bombardment arises largely from the motion of the vehicle through the ambient environment. However, enhanced solar activity and artificial environments associated with disturbed nuclear atmospheres and directed energy beams may increase the energy and intensity of the bombarding particles.

Over a wide range of bombarding energies, particle and photon interactions with surfaces have been shown to result in the efficient desorption of surface atoms and molecules. Many of these are desorbed in excited states which subsequently emit characteristic infrared, visible, and ultraviolet radiation. We will review recent work on this topic and discuss future studies of ion-, electron-, and photon-induced erosion and glow phenomena.

Photon Emission from Ion and Neutral Particle Impact on Surfaces

In the experimental observations to be treated below, three distinct kinds of collision-induced optical radiation have been identified.

The first of these is line radiation due to sputtering with simultaneous excitation. The interaction of the impinging ion or neutral beam with the surface results in the sputtering of neutral atoms, neutral molecules, and ions from the surface. A significant portion of the sputtered particles leaves the surface in excited electronic states which then decays and gives rise to optical line radiation characteristic of surface constituents [Tolk et al., 1977].

The second kind of radiation observed has a similar nature but arises from backscattered excited beam particles which have escaped the surface after having experienced collisions in the bulk material [Leung et al., 1978]. To the extent that the momentum-changing collisions do not effect the final excited state configuration of the emerging particles, this class of phenomena is identical to the beam foil radiation phenomenon. Studies of backscatter radiation provide more complete information on final states than conventional charge state measurements and give important insights into the nature of the interaction of the emerging particle with the surface.

The final and perhaps least understood type of radiation is the broad continuum of radiation that is observed from many of the solid materials studied. In the case of metals, for a given beam projectile at a given energy, the shape of the continuum is observed not to change for a variety of metal surfaces [White et al., 1976]. For insulators, the shape of the continuum as a function of wavelength is entirely characteristic of the material and independent of the beam particle species. An important conclusion from these studies is that the collision participants, both the solid itself as well as the escaping atomic and molecular fragments, in general are in excited states following the collision interaction. The collision participants may then produce the observed photons by radiative decay or may undergo radiationless de-excitation processes such as Auger de-excitation.

Metallic Targets

The spectra of radiation observed when Ar^+ ions at 4000 eV impact on Ni and Cu targets are shown in Figure 1. Most of the prominent lines in these spectral scans have been identified as arising from low-lying energy levels of neutral Ni and Cu, sputtered off the surface in excited states by the incident ion beam. In addition to spectral lines from the surface target materials, radiation is also often observed which is characteristic of surface contaminants [Tolk et al., 1973]. The molecular radiation centered at 4300 Å and 3900 Å has been identified as arising from the $\text{A}^2\Delta \rightarrow \text{X}^2\Pi$ and $\text{B}^2\Sigma - \text{X}^2\Pi$ electronic transitions of the CH molecule. This radiation is believed to originate from collisional excitation of adsorbed hydrocarbon surface contamination. The prominent line which is often observed at approximately 5900 Å is the NaD line doublet which is assumed to arise from sodium contaminants deposited on the surface. The surface can be cleaned to such an extent that the contaminant radiation is negligible by prolonged exposure (approximately 20

minutes) to a 3-keV argon ion beam or by heating the target.

Our measurements show that for metallic targets, beams of neutrals and ions (of the same species) produce photons due to sputtering with equal efficiency. Low-velocity ions with sufficiently large ionization potential impacting on a metal surface are neutralized by non-radiative processes several angstroms in front of the surface, well before the sputtering interaction occurs. It is reasonable then to assume that the radiation which results from the sputtering interaction should be the same for beams of ions or neutrals at the same velocity. This assumption has been verified experimentally using a bolometer to independently measure the neutral "current." These results consequently suggest a means of directly measuring neutral beam flux in the low-energy region. It follows from the above discussion that the ratio of the intensity of the optical line radiation produced when a metallic target is bombarded with neutrals to that produced when the same target is bombarded with ions is equal to the ratio of the neutral to ion fluxes thus leading to a direct measurement of the neutral "current." In principle, this technique could also be extended to non-metallic surfaces using a more complicated calibration scheme.

Insulator Targets

The spectral distribution of radiation arising from excited sputtered particles due to the impact of nitrogen molecules (N_2) at a beam energy of 3.5 keV on aluminum oxide (Al_2O_3), lithium fluoride (LiF), and quartz (SiO_2) is shown in Figure 2. Optical scans taken using neutral beams of neon, argon, and other heavy particles give similar results. Neutral beams rather than ion beams are used for the bombardment of insulators in order to avoid ion beam energy decrease and defocusing due to charge buildup on the insulator surface. Ion beams may also be used, however, if the insulator surface is bathed in electrons emitted from a nearby heated filament. In Figure 2, the more intense lines are identified as arising from the decay of excited states of neutral aluminum, lithium, silicon, and hydrogen. Because the line widths are found in these experiments to be equal to the instrumental resolution (about 1 angstrom), we may assume that the radiation originates from individual atoms and molecules which have been sputtered off the surface in excited states which subsequently decay by photon emission. The Balmer lines of neutral hydrogen are believed to arise from the sputtering of surface contaminants.

For all cases studied--metals, semiconductors and insulators--optical radiation has been observed due to sputtering with simultaneous excitation. However, in the insulator case, the excitation efficiency is observed to be much larger than for metals. For the case of metals, typical prominent lines are estimated to have excitation efficiencies of the order of 10^{-5} (photons per incident ion) while in the insulator case, the excitation efficiencies are measured to be two or three orders of magnitude higher [Tolk et al., 1977].

Optical Radiation from Electronically Desorbed Particles

For the case of heavy-particle induced sputtering as discussed above, understanding the influence of surface parameters on the final state of sputtered particles is complicated by the fact that the ejection of atoms and molecules results from both electronic and momentum changing processes. Electron- and UV photon-stimulated desorption of atoms and molecules, on the other hand, involves only electronic interactions.

Even though it is known that the most abundant products of electronically induced desorption are neutral atoms and molecules, most studies have involved desorbed ions. This is due primarily to the ease of detection of ions. In only a few cases have neutrals desorbed by electron and photon impact been directly studied.

It is useful to describe the mechanisms of electron and photon-induced desorption as a three-stage process: (1) the initial deposition of electron energy by, for example, the creation of a hole, two holes, an exciton, or a defect; (2) a fast electronic rearrangement leaving a surface atom or group of atoms in a localized repulsive or energetic state; and (3) further particle-surface electronic interaction as the atom, or molecule, or cluster leaves the surface. Although not treated here, recent observations of strong elliptic polarization of optical radiation following grazing incidence of 9-keV protons on crystal surfaces contribute unique information on stage (3) electronic processes [Tully et al., 1981]. Studies of these phenomena promise to provide new insight into the electronic aspects of atomic collisions in solids [Tolk et al., 1981b]. In this paper we discuss recent measurements of electronically desorbed neutrals obtained by observing optical radiation which arises from neutrals desorbed in excited states.

Electron Stimulated Desorption (ESD) of Excited Particles

Although it is now generally accepted that the most abundant products of desorption from surfaces induced by electronic transitions, stimulated by energetic electrons or UV/soft x-ray photons, are neutral atoms and molecules, only a very few results have been published about neutral desorption. These experiments confirm the leading role of neutrals in the desorption process.

Our approach to the detection of desorbed neutrals is based on analysis of the optical radiation emitted by decays after desorption [Tolk et al., 1981a]. The experimental equipment included an ultrahigh vacuum chamber, a primary excitation source, and an optical detection/analysis system with a monochromator and computer-controlled data processing. Initially, the excitation source was an electron beam. Figure 3 shows spectra of atomic and molecular radiation emitted by desorbed atoms and molecules from NaCl, NaF, and LiF surfaces, principally from excited alkalis, hydrogen, OH, and an unidentified molecular species.

In marked contrast to ion bombardment and gas discharges, the only sodium and lithium radiation detected in these experiments are first resonance lines. This indicates that for alkali halides there exists a strong nonstatistical state selection mechanism of an as-yet undetermined nature. Energy-dependent measurements show

onsets correlated to core hole formation relating to the initial energy deposition process. Electron-stimulated erosion of alkali halides is usually attributed to the creation of defects which results in the ejection of halogen atoms and leaves excess alkali atoms to desorb thermally from the surface. This does not appear to be adequate to explain the emission of excited neutrals. It is likely that this latter process involves the creation of a long-lived localized surface excitation, perhaps an exciton, which results in ejection of a surface atom and in addition supplies the excited electron.

Photon Stimulated Desorption (PSD) of Excited Particles

Desorption of excited particles was recently observed when UV photons from the University of Wisconsin synchrotron storage ring, with energies of 40-200 eV, were incident on alkali-halide surfaces [Tolk et al., 1982]. As shown in Figure 4 photon energy dependent measurements were taken of optical radiation arising from the decay of desorbed excited Li atoms. These data are compared with PSD measurements of positive ions from the same LiF sample. Both measurements showed pronounced energy-dependent structure similar (though not identical) to soft x-ray absorption coefficient measurements also presented in Figure 4. It should be noted that the yield of excited neutrals was measured to be at least 3 orders of magnitude greater than the corresponding yield of desorbed ions. Similar to the ESD case, only the first resonance level is observed. In light of these observations, a plausible three-step desorption scheme for excited neutrals may be hypothesized [Tolk et al., 1983, 1984]: (1) The incoming photon creates a core or valence excitation near the surface which provides electronic energy to the system. (2) One or a series of secondary electronic processes occur, resulting in a localized valence excitonic state, which leaves the surface alkali atom in a highly energetic or repulsive state. (3) As the alkali atom departs, the lowest excited state is preferentially populated because it is both at lower energy and more localized than the higher excited states.

Laboratory Studies of Spacecraft Glow

At Vanderbilt University, we have initiated studies of the dynamics of particle- and photon-beam interactions which lead to surface erosion and glow phenomena, emphasizing materials and surface conditions relevant to spacecraft in the near-Earth environment. This research uses facilities available at Vanderbilt and at the University of Wisconsin synchrotron storage ring for studying the interactions of directed beams of ions, neutrals, electrons, and UV photons with well-characterized surfaces under carefully controlled vacuum conditions.

Work is progressing toward the development of a high-flux beam of energetic neutral oxygen and nitrogen atoms using an existing ion source at Vanderbilt to compare ion bombardment with corresponding neutral bombardment on relevant surfaces. Desorption experiments are also in progress on metallic surfaces with controlled doses of relevant adsorbates (e.g., N_2 and O_2), to ascertain changes in surface electronic and bonding properties induced by contaminants. Finally, experiments on possible synergistic effects--as in simultaneous ion-electron and ion-photon bombardment--are now feasible and will

be carried out in the near future.

Conclusions

As discussed above, when particles impact on surfaces, many complex interrelated processes occur as the incident energy is transformed into electronic and sometimes thermal excitations. Previous studies of electronically-induced desorption have shown much of the incident energy may be channeled into bond-breaking and desorption processes leading to ejection of surface atoms and molecules from metal oxides and insulators. Thus, electronic, chemical, and thermal processes stimulated by energetic beams can play a major role in surface modification and damage, through erosion, changes in tribological properties, and migration of electronically-induced defects. The primary effort is to understand the fundamental mechanisms underlying these processes. These studies will generate an increasingly detailed microscopic view of the dominant modes through which incident energy is absorbed, localized, and redirected to desorption. This, in turn, leads to a comprehensive macroscopic picture of material ejection, erosion, and ablation from surfaces and of the associated optical emissions.

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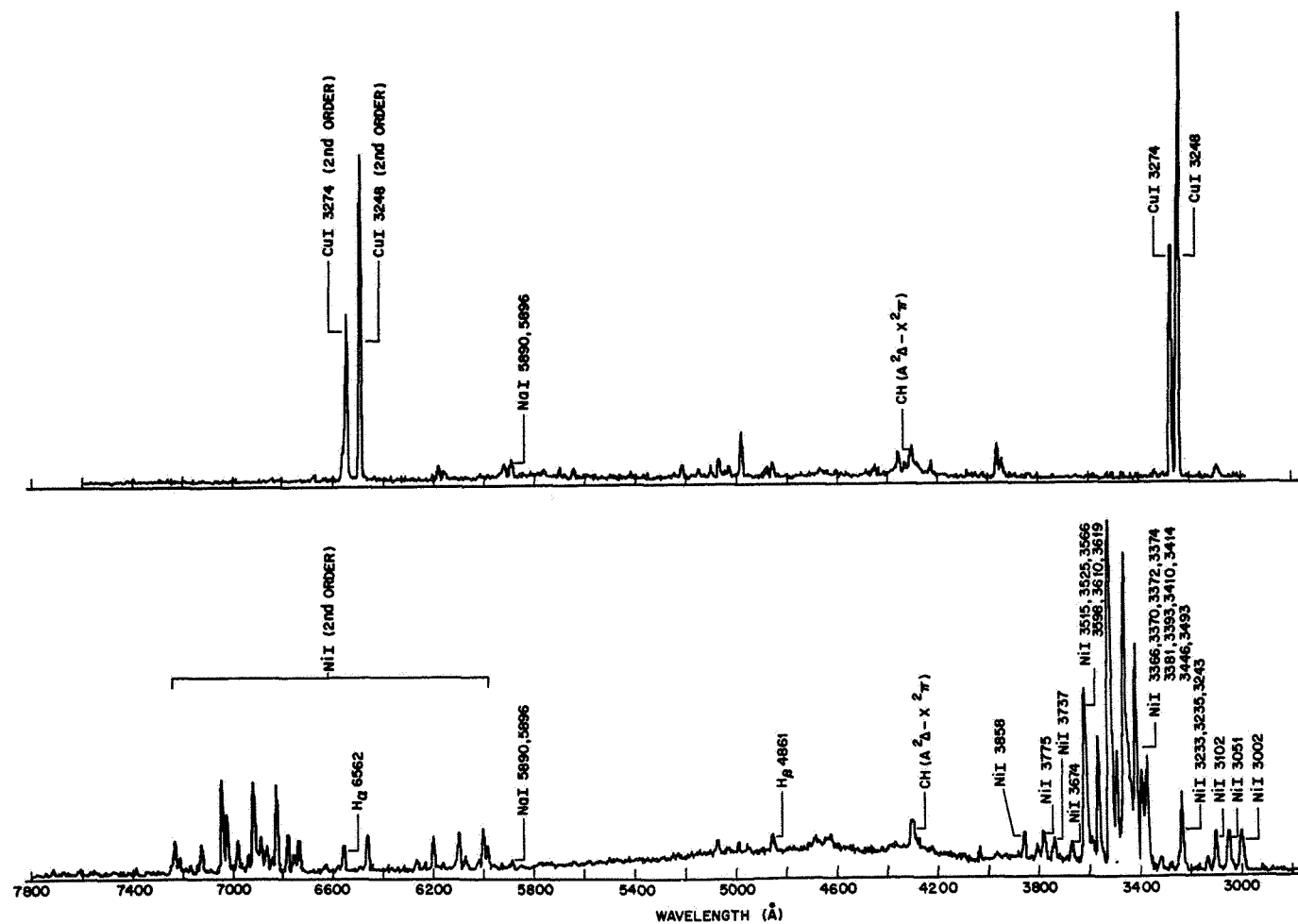


Fig. 1. Spectra of radiation produced by the impact of Ar^+ (at 4 keV) on copper (top) and nickel (bottom). Lines arising from excited states of sputtered copper, nickel, and various contaminants are observed in this wavelength interval.

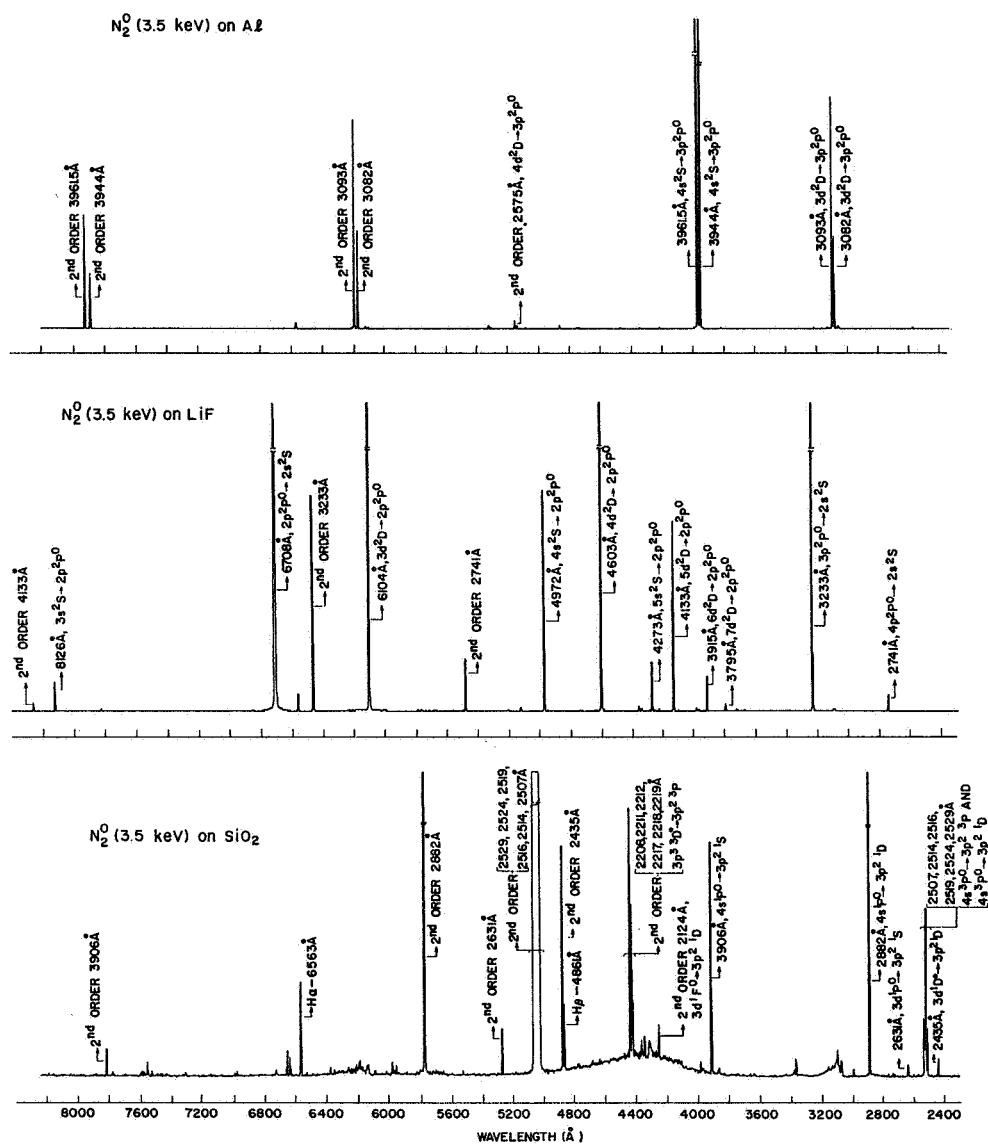


Fig. 2. Spectrum of radiation produced by the impact of N_2^+ (3.5 kiloelectron volts) on Al_2O_3 , LiF, and SiO_2 . Lines arising from excited states of neutral aluminum, lithium, and silicon are observed in this wavelength interval. The wavelength and electronic transition are indicated beside each line. Two Balmer lines of neutral hydrogen, H_α and H_β , are observed on the SiO_2 scan.

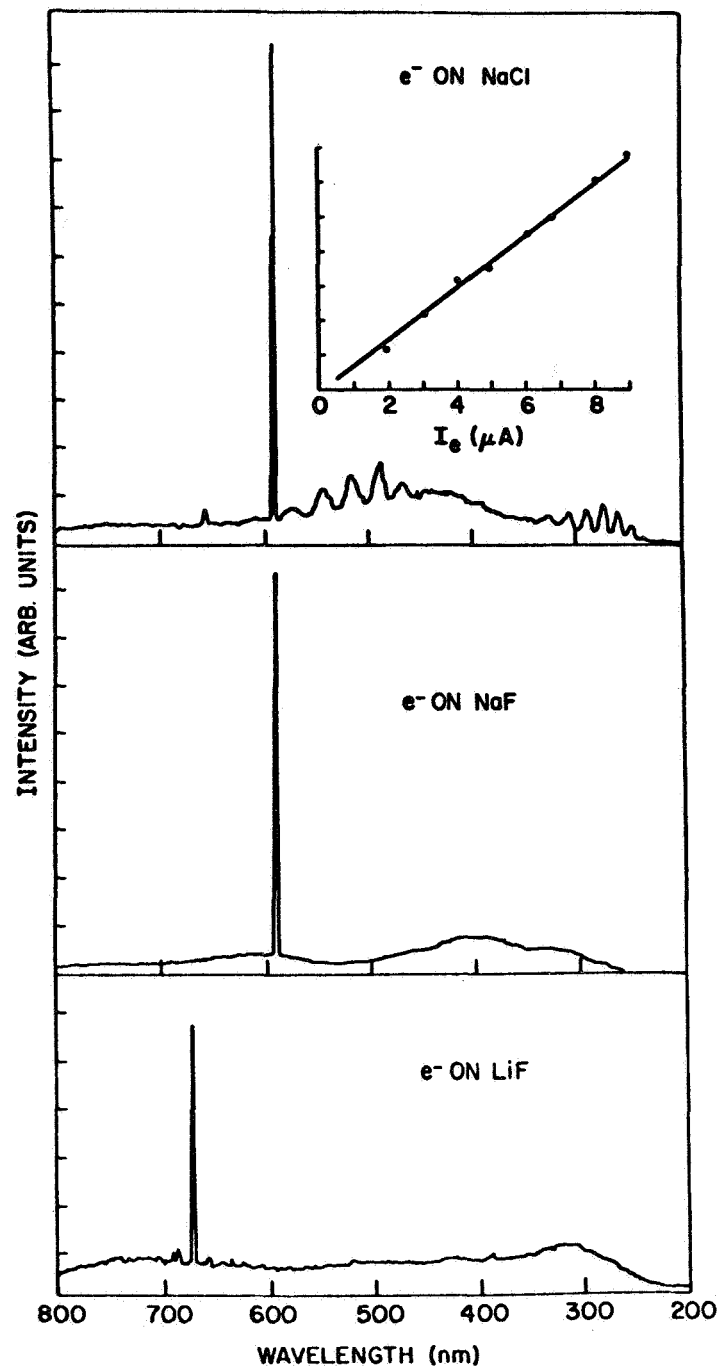


Fig. 3. Spectra of radiation produced by 1-keV e^- impact of NaCl, NaF, and LiF, obtained at approximately 90° to the surface normal. The inset shows the linear behavior of the intensity of the NaD line as a function of incident e^- current. A straight line has been drawn through the data points.

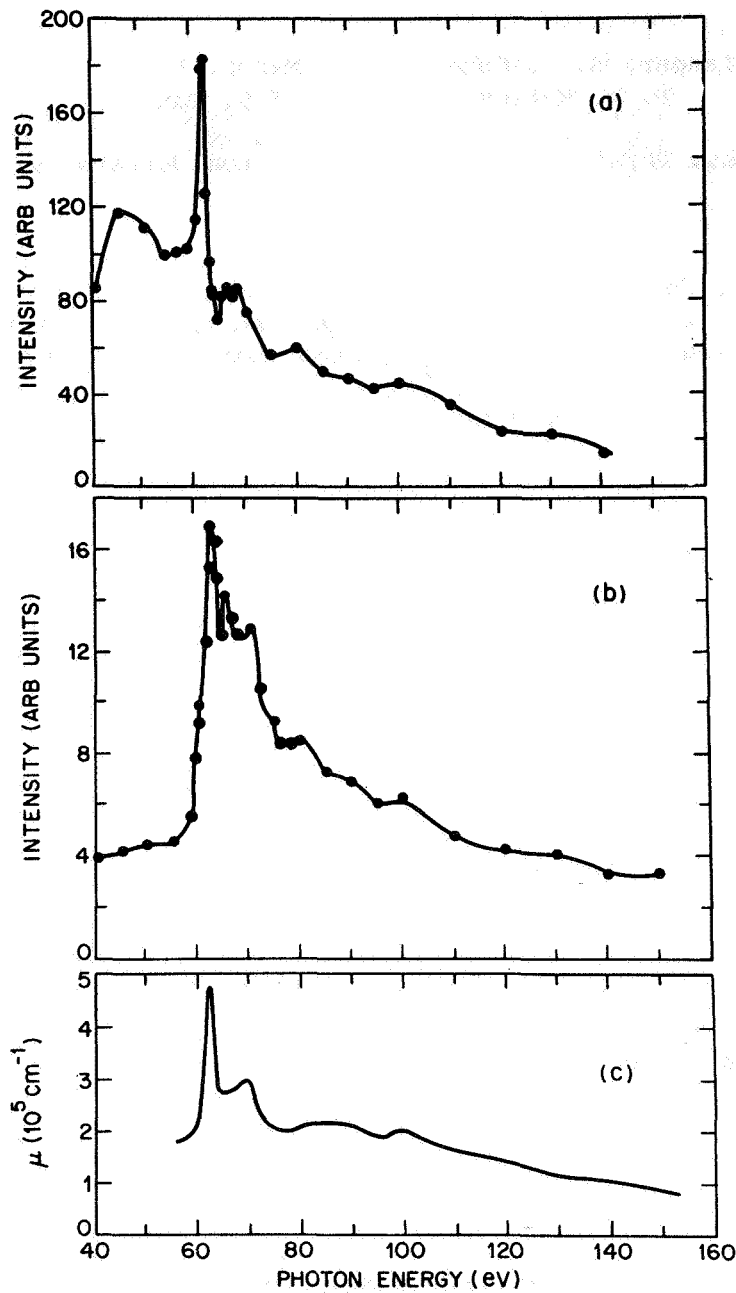


Fig. 4. (a) Li^* (670.7 nm) optical emission dependence on soft x-ray energy using a (100) single-crystal LiF sample at room temperature. (b) Positive-ion yields as a function of incident photon energy using the same sample at about 250 °C. (c) Photon absorption coefficient measurements.